Isotherm Testing:
Procedures and Application of Results

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Terminology

- (ad)sorption ⇨ accumulation
  @ solid/solvent interface
- (ad)sorbent ⇨ solid phase material
- (ad)sorbate ⇨ target compound(s)
  - ☐ arsenate (or arsenite) ✓
  - ☐ single vs. multi-sorbate
    - interferants
    - competition
- solvent ⇨ water
- knowledgebase ⇨ activated carbon + organics

Adsorbent Forms and Properties

- Granular vs. Powdered
  - □ Fixed Bed vs. Slurry Reactor (or Membrane)
- Porous vs. Non-Porous
  - □ e.g., GFH vs. SMI
  - □ Kinetics
- (Specific) Surface Area (m^2/g)
- (Surface) Charge (pH_{ZPC})
- Site Density ($\#/nm^2$)
- Mineralogy
  - □ Crystaline vs. Amorphous
  - □ Various Iron Oxides, etc. vs. Ion Exchange Resins
  - □ Strictly Adsorbent vs. Reactive media (e.g., MnO_2)

Influential Factors

- ## Temperature
  - ☐ Exo- versus Endothermic ⇨ *Isotherm*
  - ☐ Exo ⇨ adsorption $\propto$ 1/temperature;

    Endo ⇨ adsorption $\propto$ temperature
  - ☐ Adsorption
    - Generally exothermic
    - But higher diffusion at higher temperature often offsets higher temperature effects

- ## pH
  - ☐ $H_2AsO_4^-$ vs. $HAsO_4^{2-}$

- ## Interferants
  - ☐ e.g., Phosphate

Mechanisms of Arsenic Adsorption

- **Physical Adsorption** ✗
  - ☐ van der Waals Forces
- **Chemisorption** ✓
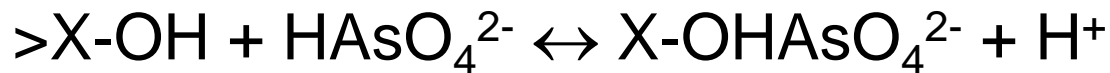 - ☐ Surface Complexation
- **Exchange Adsorption** ✓
  - ☐ Ion Exchange

Adsorption Mechanisms

- **Chemisorption:**
  - ☐ Ligand (L) Exchange

    $>X\text{-}OH + L^- \leftrightarrow >X\text{-}L + OH^-$

  - ☐ Surface Complexation

    $>X\text{-}OH + HAsO_4^{2-} \leftrightarrow X\text{-}OHAsO_4^{2-} + H^+$

- **Exchange Sorption:**
  - ☐ $>X\text{-}Cl + L^- \leftrightarrow >X\text{-}L + Cl^-$

- **Influential Factors**
  - ☐ pH: $H_2AsO_4^-$, $HAsO_4^{2-}$
  - ☐ pH_{ZPC} of Adsorbent; if $pH < pH_{ZPC}$, "+"
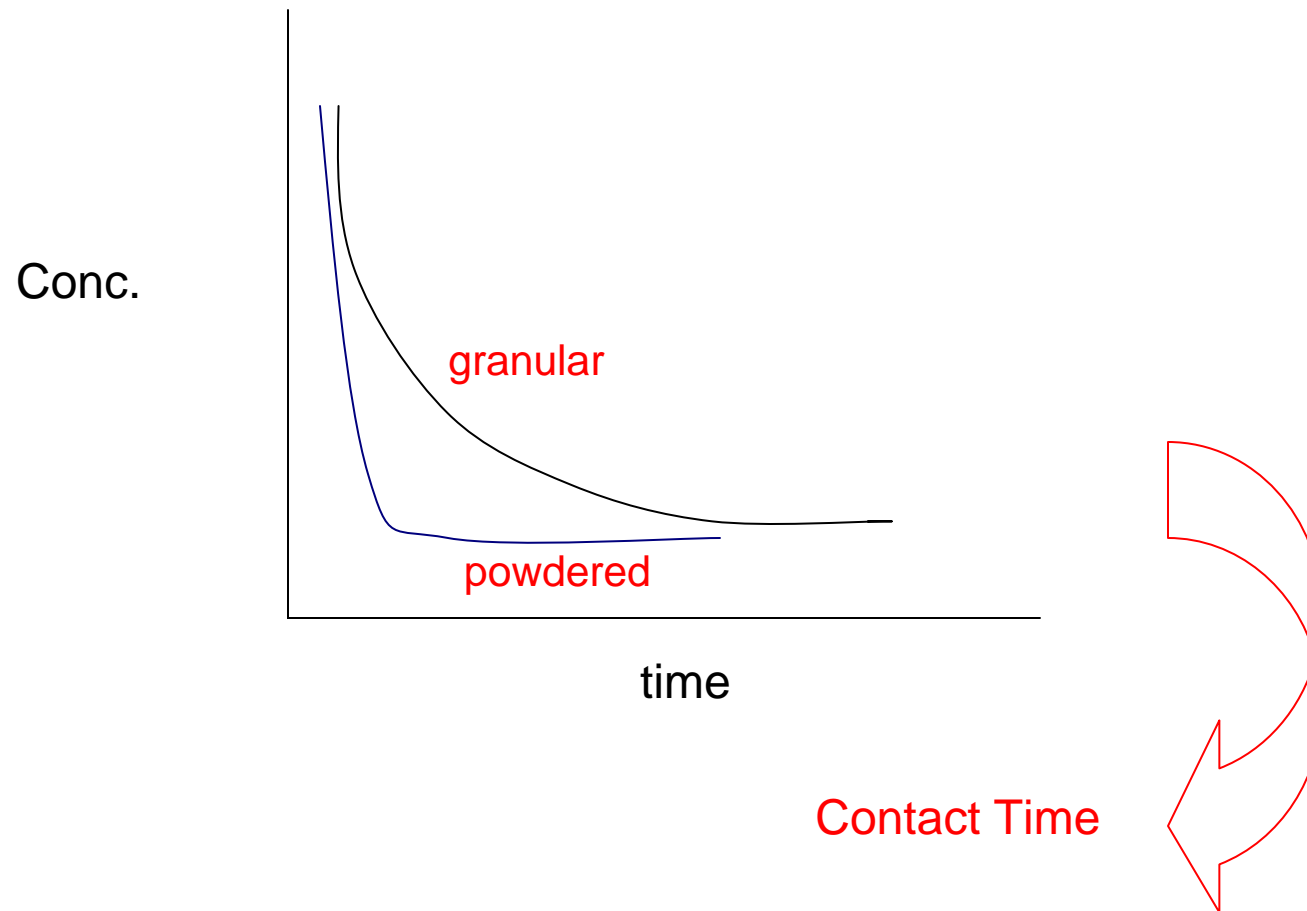 - ☐ Inner (bond) vs. Outer Sphere Complexes (ion pair)

Mass Transfer Steps

- **(External) Film Diffusion**
- **(Internal) Pore and/or Surface Diffusion**
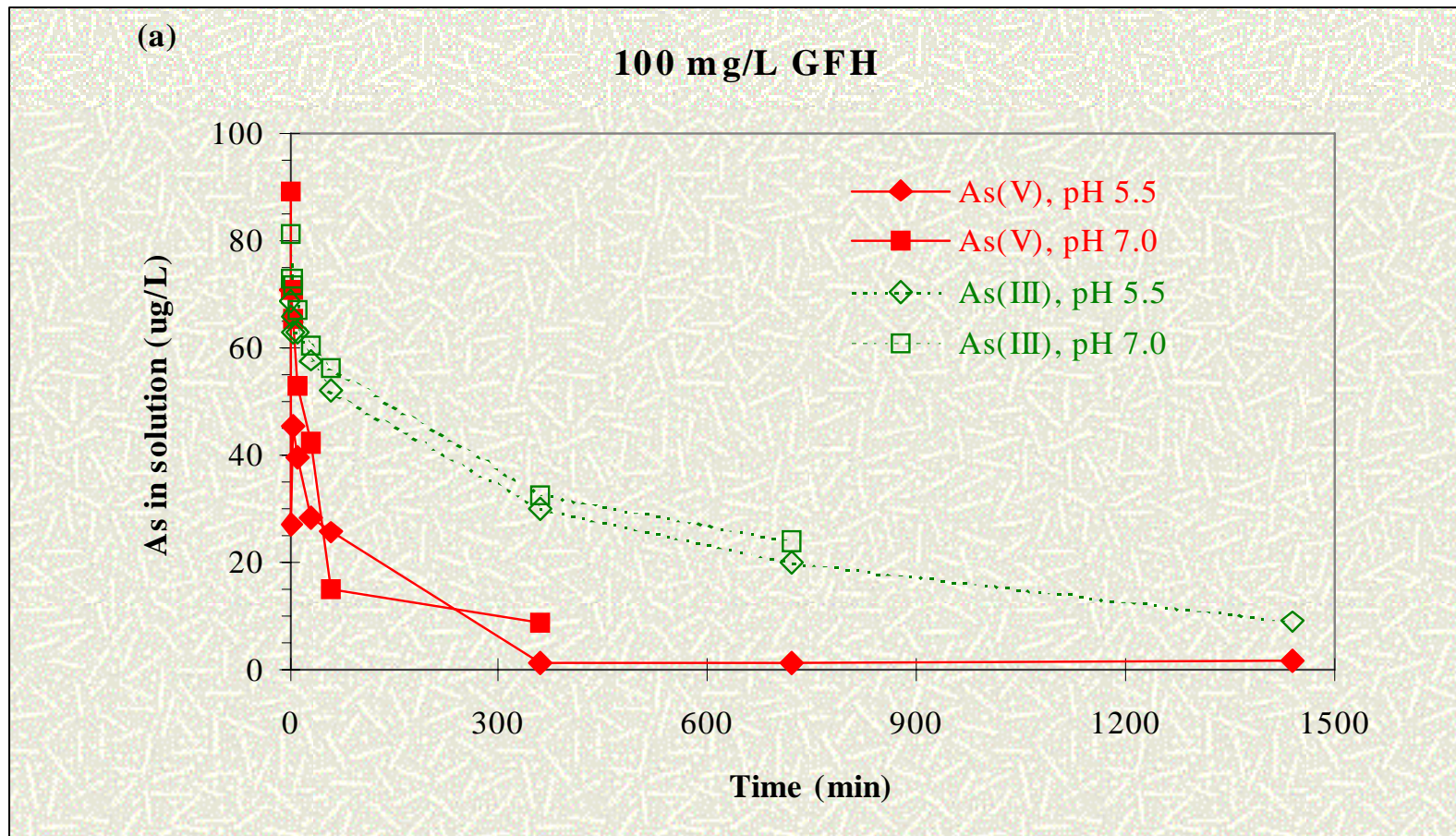 - ☐ Generally Rate-Limiting
- **Surface Reaction**

Kinetics

Bulk (fast) | Film (slow) | Intraparticle (slow) Adsorption (fast)

Kinetics

Conc.

granular

powdered

time

Contact Time

Kinetics

(a)

100 mg/L GFH

As in solution (ug/L)

- As(V), pH 5.5
- As(V), pH 7.0
- As(III), pH 5.5
- As(III), pH 7.0

Time (min)
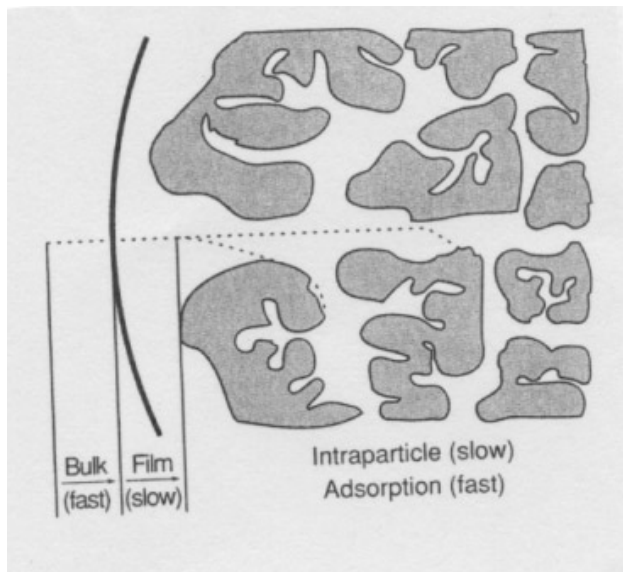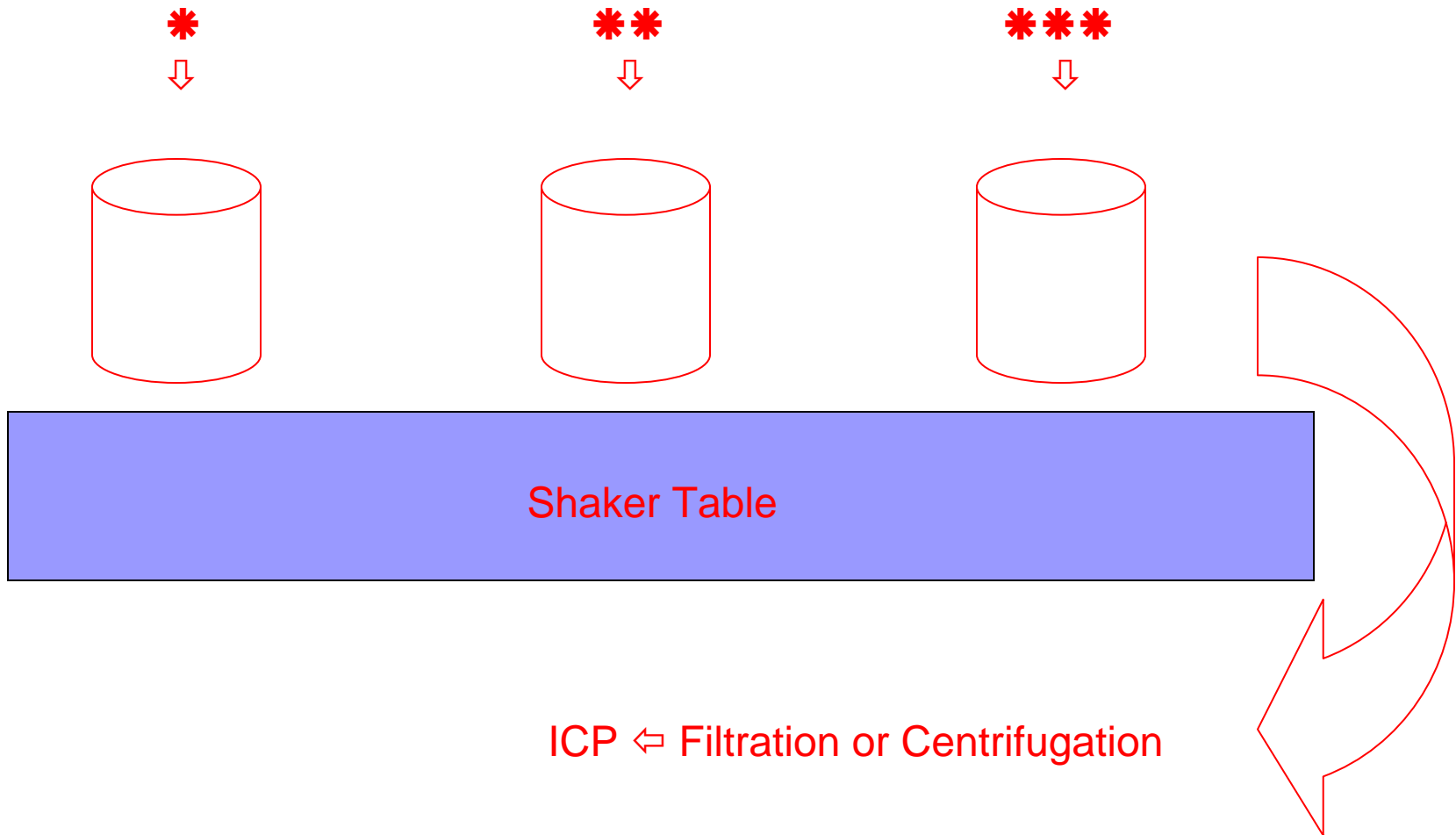
Other Studies: up to 96 hours

Bottle Point Isotherms

Bottle Point Experiments

- Concentration Constant ⇨ Vary Adsorbent
  - natural water

- Adsorbent Constant ⇨ Vary Concentration
  - e.g., synthetic water

- Multi-Adsorbate
  - C_0 of arsenic and interferant affects isotherm

(Equilibrium) Isotherms

- $q = x/m = (V(C_0 - C))/m$
  - $q \Rightarrow$ solid phase conc. (e.g., ug/mg)
  - $C \Rightarrow$ equil. water-phase conc. (e.g., ug/L)
    - Initial (C_0) vs. Equilibrium (C)
  - $m \Rightarrow$ adsorbent concentration (e.g., mg/L)
  - $V \Rightarrow$ volume (e.g., L)
  - $x \Rightarrow$ mass adsorbed (e.g., ug)
- Batch Equilibrium Tests
  - Equilibration Time:
    - Powdered $\Rightarrow$ minutes to hours
    - Granular $\Rightarrow$ hours to days
    - Pulverize granular media?
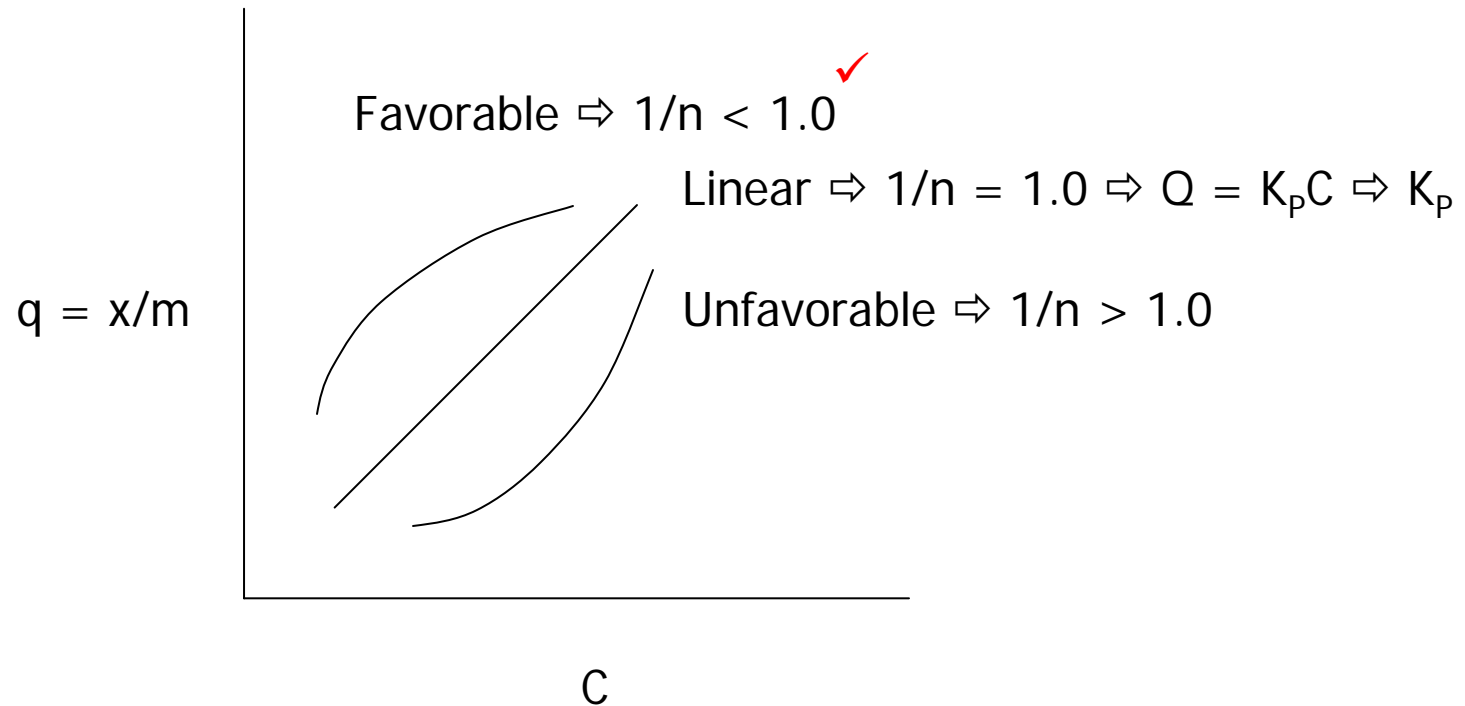
Activated Alumina Isotherms
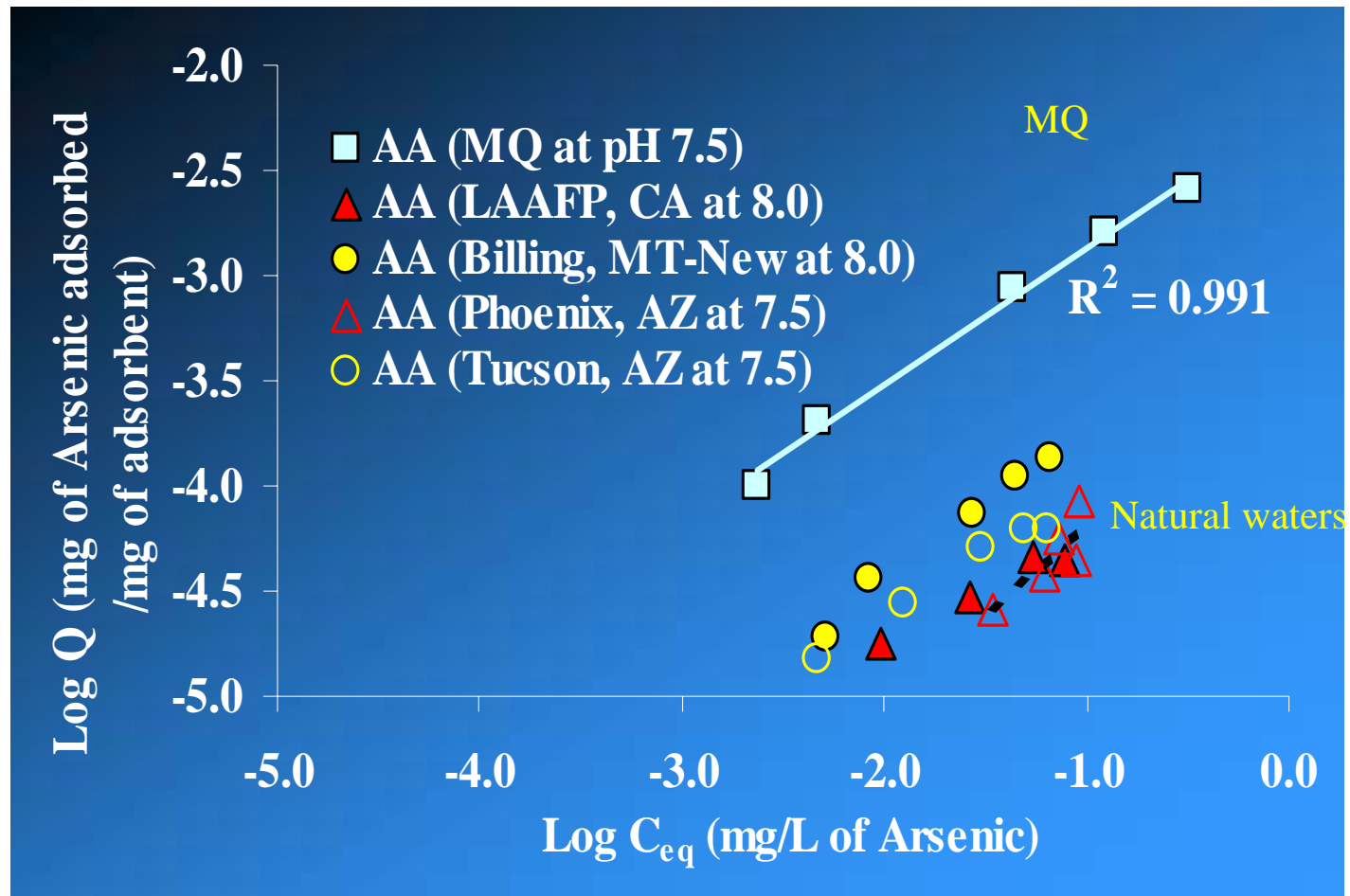
Isotherm Equations

- Freundlich
  - Empirical; good data fit of intermediate range data
  - $q = K_F C^{1/n}$ (or $q = KC^n$ in Europe)
  - $q \Rightarrow$ solid phase conc. (ug/mg, moles/g, etc.)
  - $C \Rightarrow$ equil. water-phase conc. (ug/l, moles/L, etc.)
  - K_F & $1/n \Rightarrow$ empirical constants
    - $K_F \Rightarrow$ capacity parameter (units!)
    - $1/n \Rightarrow$ index of „favorable" vs. „unfavorable" adsorption
- Langmuir
  - Theoretical; good fit of higher and lower range data
  - $q = (Q_{max}K_L C)/(1 + K_L C)$
  - $Q_{max} \Rightarrow$ max. surface conc.
    - indicative of „monolayer" coverage or site saturation ✓
  - $K_L \Rightarrow$ constant

Favorable vs. Unfavorable Adsorption

Favorable $\Rightarrow$ 1/n < 1.0 ✓

Linear $\Rightarrow$ 1/n = 1.0 $\Rightarrow$ Q = K_PC $\Rightarrow$ K_P

$q = x/m$

Unfavorable $\Rightarrow$ 1/n > 1.0

C

Determination of Isotherm Constants – cont.

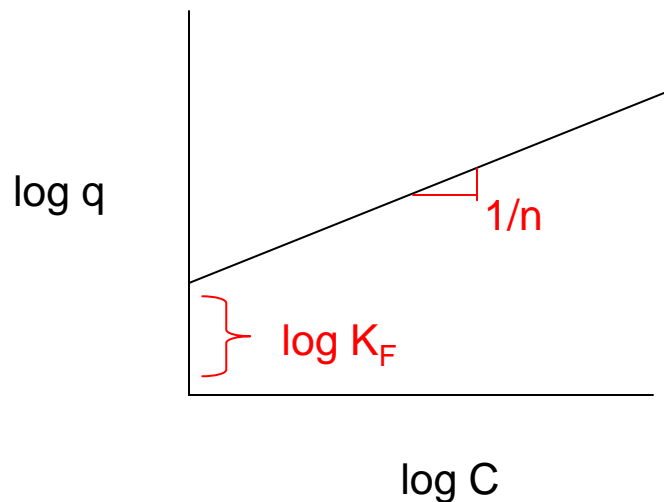- ## Linearization of Freundlich Equation

  - $\log q = \log K_F + 1/n \log C$

  - log-log plot

    - Intercept $\Rightarrow K_F$
    - Slope $\Rightarrow 1/n$

Determination of Isotherm Constants – cont.

- **Linearization of Langmuir Equation**
  - $1/q = 1/Q_{max} + (1/bQ_{max})(1/C)$
  - Plot of $1/q$ vs. $1/C$
    - Intercept $\Rightarrow 1/Q_{max}$
    - Slope $\Rightarrow 1/K_L Q_{max}$

Adsorption Capacity

- q vs. C
  - ☐ q_{eq} vs. C_{eq}
  - ☐ q_0 vs. C_0
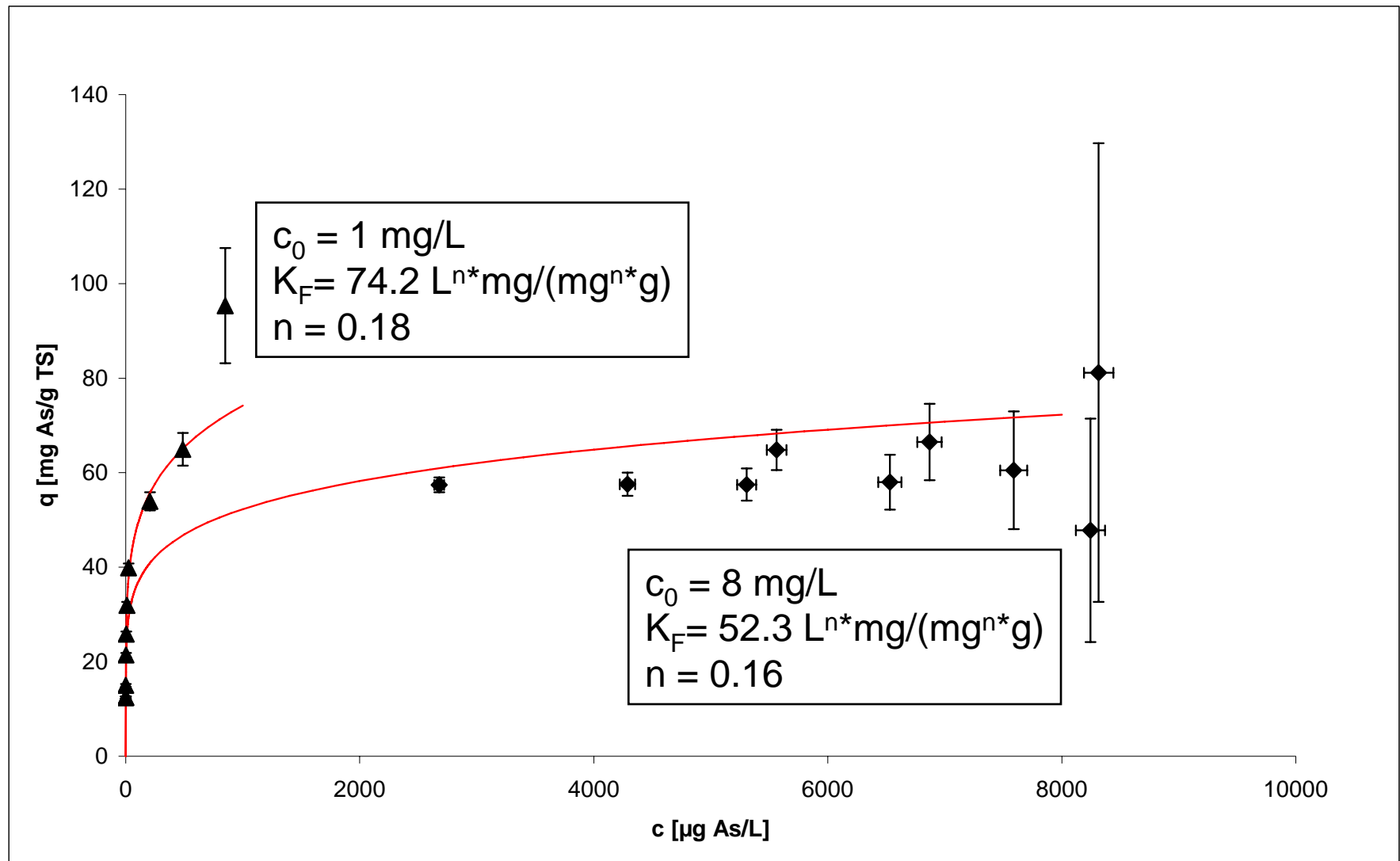 - ☐ q_{10} or q_{50} vs. C = 10 or 50 ug/L
  - ☐ mass based q (ug/mg)
    vs. surface area based q (ug/cm^2)

A *Robust* Isotherm

- **Lower Level Resolution**
  - ☐ Adsorbate Limited

- **Higher Level Resolution**
  - ☐ Adsorbent Limited

Isotherm: Higher and Lower Concentration Ranges

$c_0 = 1$ mg/L
$K_F = 74.2$ L^n*mg/(mg^n*g)
$n = 0.18$

$c_0 = 8$ mg/L
$K_F = 52.3$ L^n*mg/(mg^n*g)
$n = 0.16$

q [mg As/g TS]

c [µg As/L]

Adsorption of Mixtures

- Multiple Adsorbates
- Reduced Single Adsorbate Capacity

Competitive Langmuir Equation

- $q_i = (Q_{max,i}K_{L,i}C_i)/(1 + \sum_{j=1}^{n}(K_{L,j}C_j))$

  - $\square$ n $\Rightarrow$ number of (ad)sorbates
  - $\square$ C_i $\Rightarrow$ equil. conc. of i sorbate in a j sorbate mixture
  - $\square$ q_i & $K_{L,i}$ $\Rightarrow$ single sorbate parameters

- For two (Ad)sorbates:
  - $\square$ $q_1 = (Q_{max,1}K_{L,1}C_1)/(1 + K_{L,1}C_1 + K_{L,2}C_2)$
  - $\square$ $q_2 = (Q_{max,2}K_{L,2}C_2)/(1 + K_{L,1}C_1 + K_{L,2}C_2)$
  - $\square$ $Q_{max,1}$, $Q_{max,2}$, $K_{L,1}$, $K_{L,2}$ $\Rightarrow$ derived from single sorbate experiments
  - $\square$ C_1, C_2 $\Rightarrow$ derived from competitive sorbate experiments
  - $\square$ q_1, q_2 $\Rightarrow$ calculated from competitive adsorption

Information Provided by Isotherms

- **Powdered Adsorbent Applications**
  - ☐ If m is specified, C = ?
    - q = x/m = (V(C_0 − C))/m = = $K_F C^{1/n}$
  - ☐ If C is specified, m = ?
    - q = x/m = (V(C_0 − C))/m = = $K_F C^{1/n}$
- **Granular Adsorbent Applications**
  - ☐ Column-mode capacity ⇨ q_0 (vs. C_0)

How does isotherm capacity relate to column capacity?
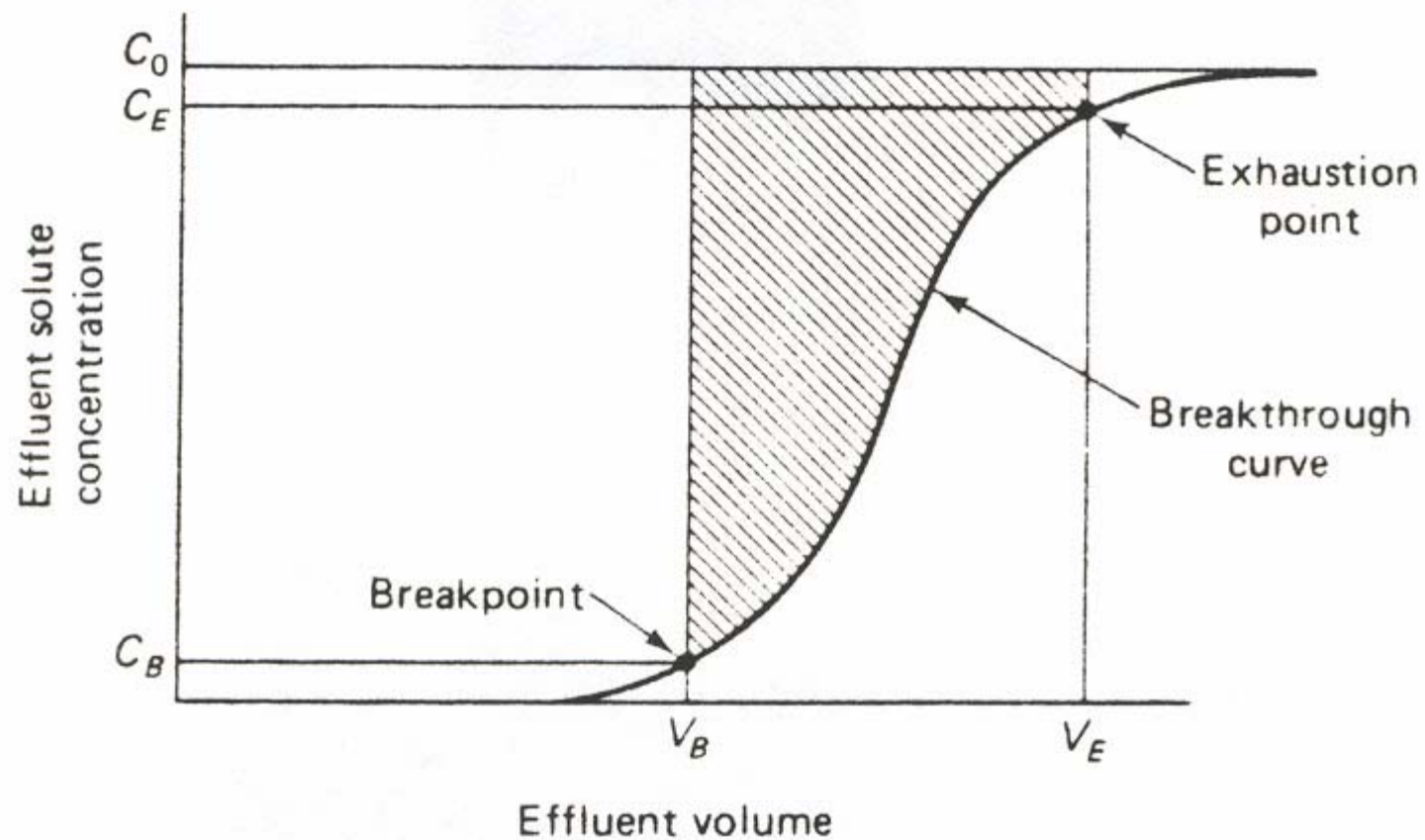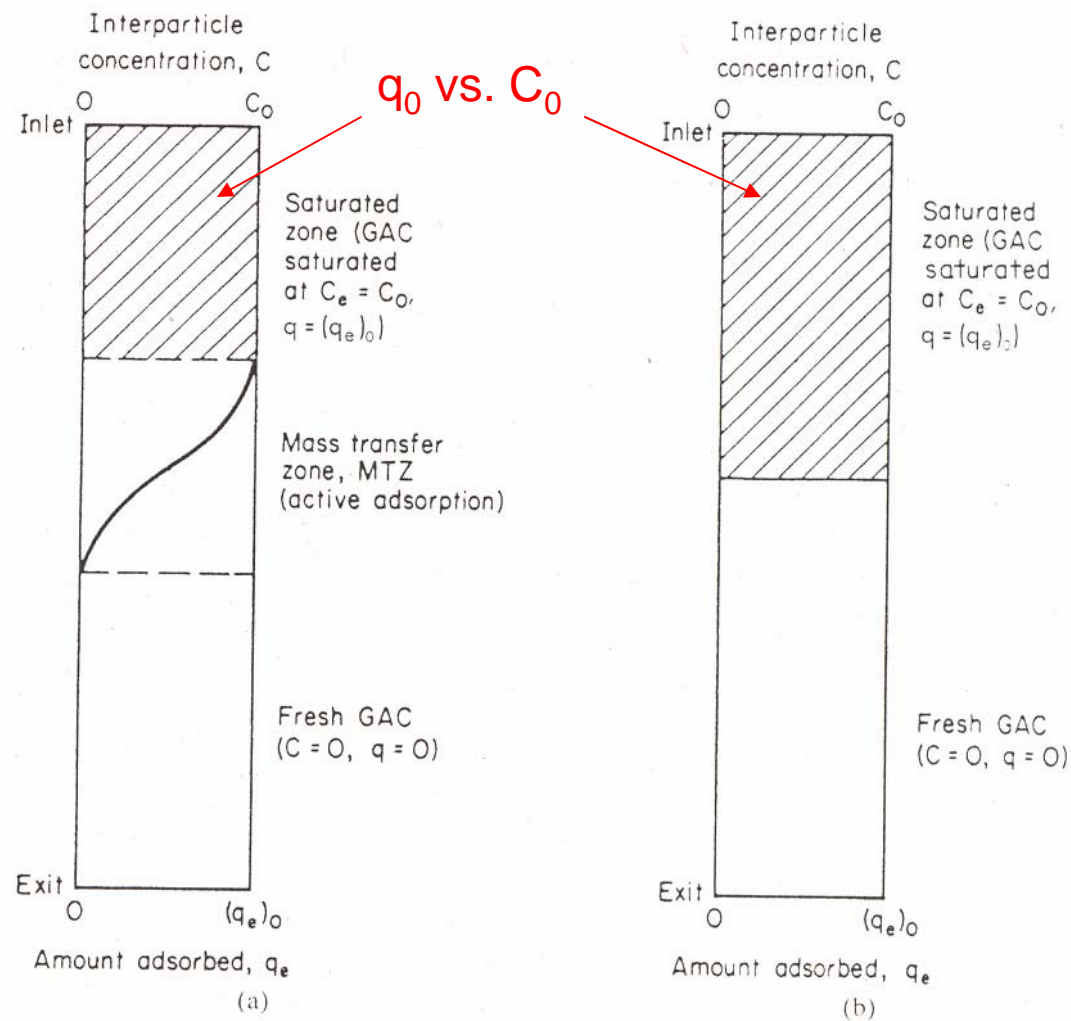
GAC Column Performance

- C(oncentration) to Breakthrough or Exhaustion vs.

  t(ime) or

  V(olume), ΣV, or

  B(ed) V(olumes), BVs $= \Sigma V / V_{empty}$

Fixed Bed Column:
Idealized Breakthrough Curve (BTC)

Adsorption Column
with (a) and without (b) MTZ

q$_0$ vs. C$_0$

(a) Interparticle concentration, C; Inlet; O, C$_O$; Saturated zone (GAC saturated at $C_e = C_O$, $q = (q_e)_0$); Mass transfer zone, MTZ (active adsorption); Fresh GAC ($C = O$, $q = O$); Exit; O, $(q_e)_0$; Amount adsorbed, q_e

(b) Interparticle concentration, C; Inlet; O, C$_O$; Saturated zone (GAC saturated at $C_e = C_O$, $q = (q_e)_0$); Fresh GAC ($C = O$, $q = O$); Exit; O, $(q_e)_0$; Amount adsorbed, q_e

Mass Adsorbed at Breakthrough or Exhaustion

- Integration of BTC: C (mg/L) vs. V (L)

$$\int_{V=0}^{V=V} (C_0 - C)\,dV$$

$$x \Rightarrow x/m \Rightarrow q$$
(with m above x/m)

$$V \Rightarrow V_B \text{ or } V_E$$

Integration of BTC
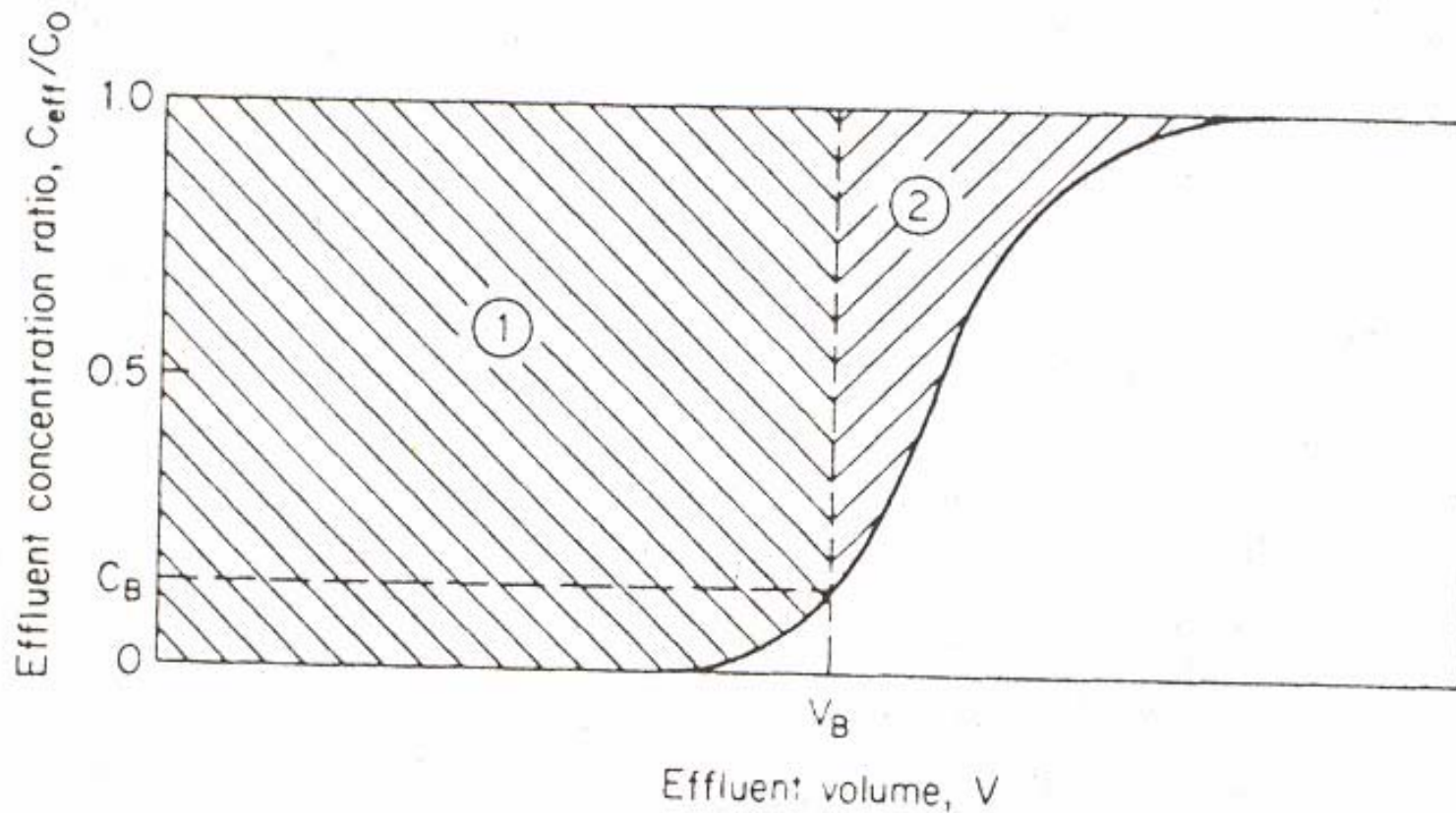
Breakthrough Capacity ⇨ ① x C_0
Exhaustion Capacity ⇨ ① + ② x C_0
Capacity Utilization (%) @ Breakthrough ⇨ ①/① + ② x 100
Stoichiometric Breakthrough @ $C/C_0 = 0.5$

Adsorbent Utilization Rate (AUR)

- AUR (mass/volume)

- AUR = $\dfrac{\text{mass of adsorbent in column}}{\text{volume treated to breakthrough, } V_B}$

- From BTC:

  AUR = $\rho_{adsorbent}$ (g/L)/BVs to breakthough

- From Isotherm:

  AUR (g/L) = $(C_0)/q_0$
  - g/L = mg/L ÷ mg/g

Adsorbent Bedlife (BVs)

- **From BTC:**
  - ☐ BVs @ breakthrough
- **From Isotherm:**

Bed-Life = q_0/C_0 x $\rho_{adsorbent}$

  - ☐ Bed-Life ⇨ BVs
  - ☐ q_0 ⇨ mg/g
  - ☐ C_0 ⇨ mg/L
  - ☐ $\rho_{adsorbent}$ ⇨ apparent density of adsorbent (g/L)
  - ☐ dimensionless = mg/g ÷(mg/L) x g/L

Summary

- Isotherms provide an equilibrium estimate of capacity

- Isotherms provide an tool for rapid screening of candidate adsorbents and interferants

- Isotherms provide insight into column capacity

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